

Capture of Hydrogen Using ZrNi

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Water, as ice, is thought to reside in craters at the lunar poles along with CH₄ and H₂. A proposed robotic mission for 2012 will utilize metal/metal hydrides for H₂ recovery. Specifications are 99% capture of H₂ initially at 5 bar and 100 °C (or greater), and degassing completely at 300 °C. Of 47 systems examined using the van't Hoff equation¹, 4 systems, Mg/MgH₂, Mg₂Ni/Mg₂NiH₄, ZrNi/ZrNiH_{2.8}, and Pd/PdH_{0.77}, were considered likely candidates for further examination. It is essential, when selecting a system, to also examine questions regarding activation, kinetics, cyclic stability, and gas impurity effects. After considering those issues, ZrNi was selected as the most promising candidate, as it is easily activated and rapidly forms ZrNiH_{2.8}. In addition, it resists oxide poisoning by CO₂, and H₂O, while some oxidation by O₂ is recommended for improved activation.²

The presence of hydrogen in the as received Zr-Ni alloy from Alfa Aesar posed additional technical problems. X-ray diffraction of the Zr-Ni powder (-325 mesh), with a Zr:Ni wt% ratio of 70:30, was found to consist of ZrH₂, ZrNiH_{2.8}, and ZrNi. ZrH₂ in the alloy presented the risk that after degassing that both Zr and ZrNi would be present, and thus lead to erroneous results regarding the reactivity of ZrNi with H₂. Fortunately, ZrH₂ is a highly stable hydride that does not degas H₂ to any significant extent

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at temperatures below 300 °C. Based on equilibrium calculations for the decomposition of ZrH_2 , only 1 millionth of the hydride decomposed at 300 °C under a N_2 atmosphere flowing at 25 ccm* for 64 hours, the longest time for pretreatment employed in the investigation. It was possible, from the X-ray results and knowledge of the Zr:Ni ratio, to compute the composition of a pretreated specimen as being 76 wt% ZrNi and the balance ZrH_2 .

A schematic drawing of the apparatus used in the investigation is presented in Figure 1. It consists of a gas delivery system (mass flow controllers, mixer, and preheater), hydride reactor (furnace and temperature controller), and monitoring instruments (pressure transducer, thermocouples with digital readouts, volumetric flowmeter, and gas chromatograph (GC)). The hydride reactor consisted of an outer heating element surrounding 2 clamshell shaped aluminum blocks that fitted tightly around the stainless tube that contained the solid reactant. The length and diameter of the bed containing the solid reactant were approximately 5 cm and 1 cm respectively. The aluminum clam shells and preheater were used to produce a uniform temperature within the reactor.

A typical experiment began by pretreating the specimen at 300 °C under a flowing atmosphere of N_2 at 25 ccm for a minimum of 16 hours to remove residual hydrogen from the $\text{ZrNiH}_{2.8}$. After pretreating the specimen the N_2 flow rate was set, unless specified otherwise, at 80 ccm, and the hydride furnace, preheater and heating tape powered to achieve the desired specimen temperature. Usually 10 to 20 minutes after the specimen was at temperature, the flow of H_2 was set at approximately 20 ccm unless stated otherwise. During an experiment, the temperatures of the gas entering and

* All volumetric flow rates, volumes H_2 sorbed and desorbed, and superficial velocities are reported at 293 K and 1 bar. Flow rates are in ccm (cm^3/min).

Diagram for H₂ Scrubbing

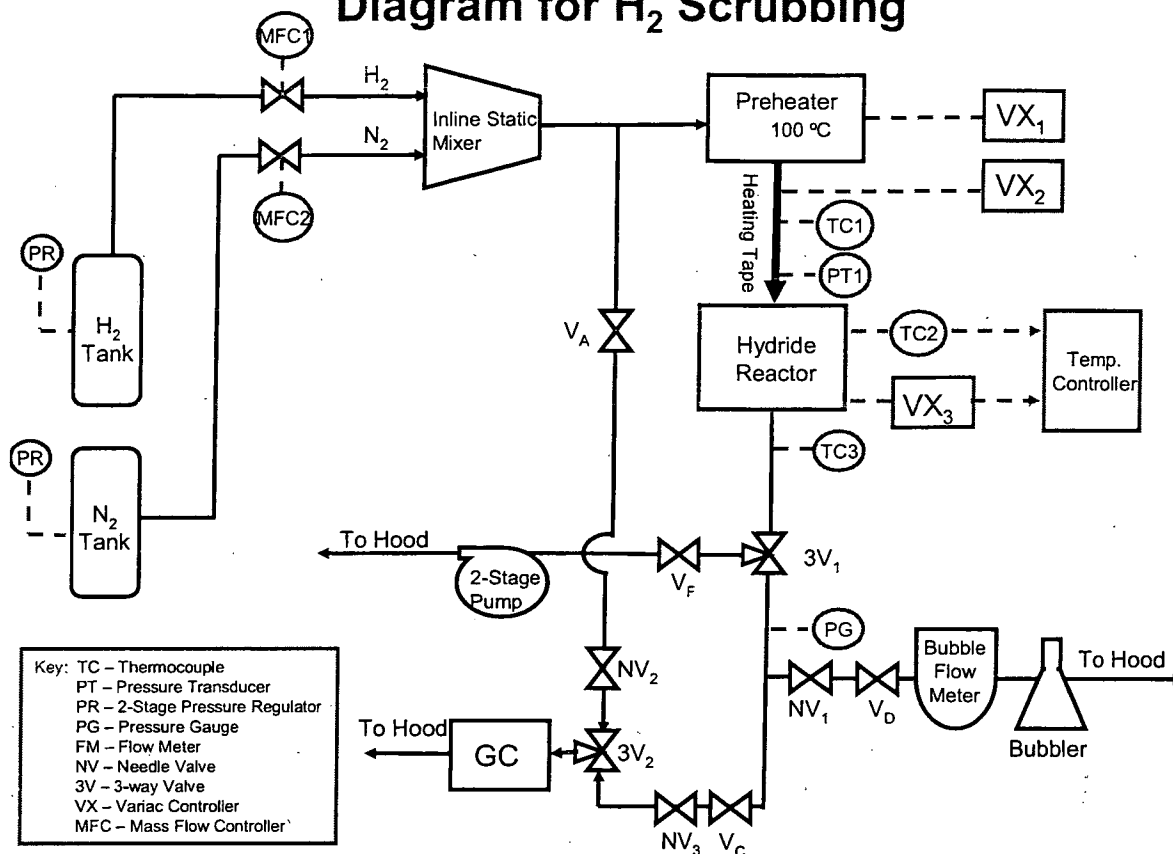


Fig. 1 – Experimental Apparatus

leaving the hydride furnace, and the temperature of the furnace itself, were monitored along with the volumetric flow rate of gas leaving the system. The transducer was used to monitor pressure upstream of the reactor, and the flowmeter (by indirect means) and GC (by direct means) were used to monitor the composition of the gas leaving the apparatus. After saturating a specimen with hydrogen, a small portion of the gas flow was diverted, from upstream of the hydride furnace, directly to the GC to obtain the composition of the inlet gas. That information was used to calculate the volumetric percent of H₂ sorbed during an experiment. After obtaining that final GC reading, power to the furnace, preheater, and heating tape was discontinued, and the system allowed to cool to room temperature before discontinuing the flow of H₂. The system was then flushed

with N₂ until the GC could no longer detect the presence of H₂, and then the power to the furnace, preheater, and heating tape restored. The furnace temperature was raised to 300 °C, and the extent H₂ evolved was followed using both the GC and the flowmeter. After degassing, the N₂ flow rate was reduced to 25 ccm and the system purged overnight at 300 °C.

Accuracy, regarding sorption and desorption results, was tested by comparing values obtained with the GC to those obtained with the flowmeter. With knowledge of the flow rates of both N₂ and H₂ entering the experimental apparatus and data obtained with

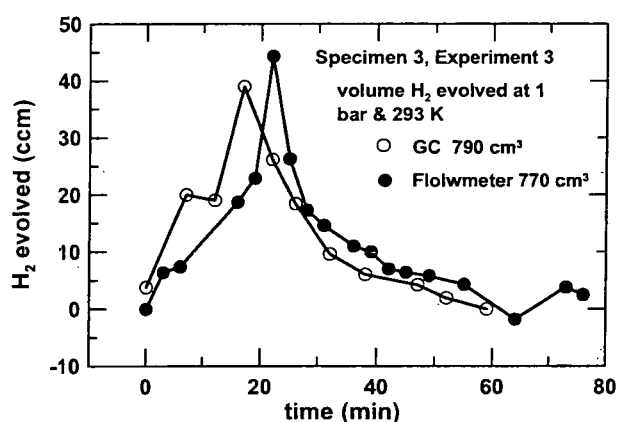


Fig. 2 – Comparison of techniques for monitoring H₂ desorption.

the GC and flowmeter, it was possible to compute the percent H₂ sorbed and, during degassing, the volume of H₂ evolved. Example of results obtained with the 2 techniques during degassing is presented in Figure 2. The comparison reveals excellent agreement between the two methods.

Experiments were run to examine the impact of process variables on activation, sorption, desorption, and structure of the reacted specimens. All specimens in this investigation self activate at a partial pressure of H₂ (p_{H_2}) equal to 0.2 bar and temperatures as low as 100 °C. Activation was also achieved at temperatures as low as 22 °C, but at higher pressures of pure H₂ (P_{H_2}). Typical results are presented in Figure 3(a) for the reaction



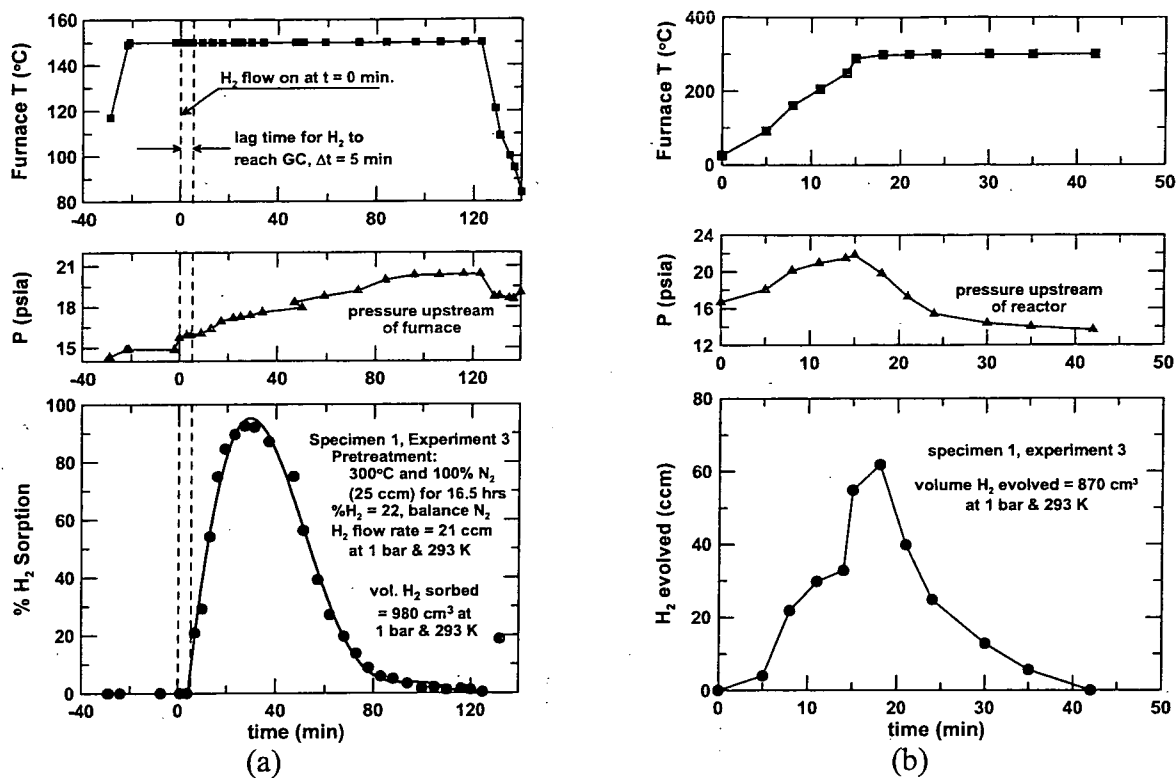


Fig. 3 Typical experimental results, (a) sorption and (b) desorption. Initial mass of as received specimen was 13.06 grams.

and for the degassing of the hydride in Figure 3(b). During an experiment, gas flowed down through a fixed bed of the powdered specimen. Resistance to gas flow through the bed increased, as indicated by the rise in gas pressure upstream of the bed as shown in Figure 3(a). The rate of increasing pressure declined as the percentage of H₂ being sorbed declined. This result suggests swelling occurs upon conversion of ZrNi to ZrNiH_{2.8}. The pressure upstream of the hydride furnace dropped as hydrogen was desorbed as shown in Figure 3(b), indicating that the swelling process is reversible. Particle dusting can occur as a result of repeated swelling and contraction, as such each specimen employed in this investigation was limited to 4 cycles. Scanning electron microscopy revealed no detectable change in particle size after 4 cycles.

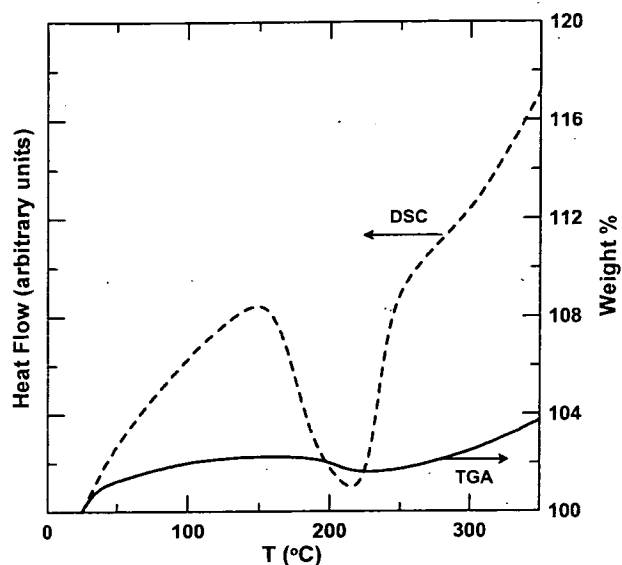


Fig. 4 – DSC and TGA results of as received material

Results of thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) presented in Figures 4 and 5 suggest that a specimen resists oxidation at temperatures up to 300 $^{\circ}\text{C}$. In Figure 4 the as received material was heated to 350 $^{\circ}\text{C}$. Decomposition of $\text{ZrNiH}_{2.8}$ (an endothermic reaction), in that material, begins at 140 $^{\circ}\text{C}$ and is complete at 260

$^{\circ}\text{C}$. This was also found true of reacted specimens. Further heating of the specimen resulted in additional weight gain. As a result of that weight gain, a second specimen, first reacted with H_2 and degassed at 300 $^{\circ}\text{C}$, was examined using both TGA and DSC. The results of that examination, presented in Figure 5, reveal that the weight gain observed in Figure 4 at temperatures above 300 $^{\circ}\text{C}$ continues at temperatures up to 800 $^{\circ}\text{C}$ with an overall weight gain of 30.5 percent. The DSC results indicate that the weight gain is due to an exothermic process that was

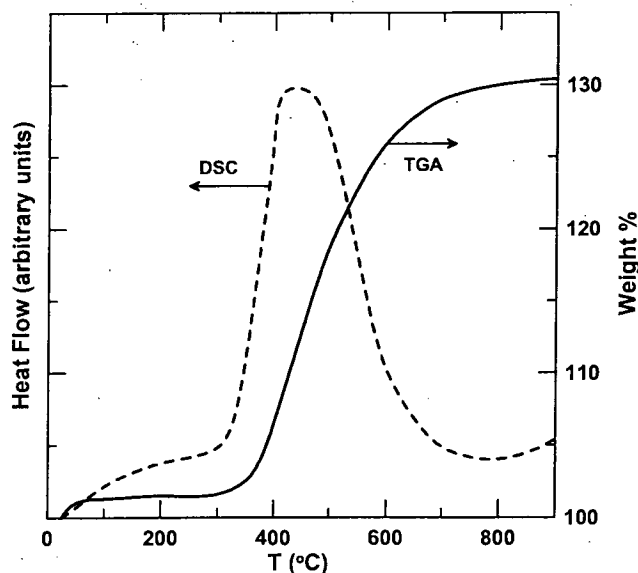


Fig. 5 – DSC and TGA results of specimen first reacted with H_2 and then degassed at 300 $^{\circ}\text{C}$.

attributed to reaction of the specimen with either O₂ impurity in the N₂ gas used with the instrument, or with N₂ itself.

Likely exothermic reactions, producing the weight percent increase observed in Figure 5, are summarized in Table I. The initial weight gain, observed at temperatures below 100 °C in Figures 4 and 5, is attributed to drag or change in buoyancy, as an inert specimen produced a similar weight gain. Thus the overall weight increase observed in Figure 5 amounts to approximately 29%. Comparison of the observed increase in wt% with those calculated for the different scenarios presented in Table I suggests that all Zr in the specimen was oxidized at temperatures above 300 °C, while Ni, a more noble metal, was not oxidized. That result suggests that ZrNi, used in sorption of H₂ will resist oxidation by O₂ up to 300 °C.

Table I Impact of Possible Reactions on Weight of Pretreated Specimen* in DSC/TGA Experiment

Reactant & Products	Reactions	Total Change in Specimen Weight (wt%)
All Zr converted to ZrN, & all H evolved as H ₂	$\text{ZrH}_2 + 1/2\text{N}_2(\text{g}) = \text{ZrN} + \text{H}_2(\text{g})$ $\text{ZrNi} + 1/2\text{N}_2(\text{g}) = \text{ZrN} + \text{Ni}$	13.2
All Zr converted to ZrO ₂ , & all H evolved as H ₂ (or H ₂ O)	$\text{ZrH}_2 + \text{O}_2(\text{g}) = \text{ZrO}_2 + \text{H}_2(\text{g})$ $\text{ZrNi} + \text{O}_2(\text{g}) = \text{ZrO}_2 + \text{Ni}$	30.8
All Zr & Ni converted to ZrO ₂ and NiO, & all H evolved as H ₂ (or H ₂ O)	$\text{ZrH}_2 + \text{O}_2(\text{g}) = \text{ZrO}_2 + \text{H}_2(\text{g})$ $\text{ZrNi} + 3/2\text{O}_2(\text{g}) = \text{ZrO}_2 + \text{NiO}$	42.4

*specimen consists of 76 wt% ZrNi and 24 wt% ZrH₂

Temperature was found to significantly impact both rate and extent of H₂ sorption. A flowing gas of H₂ and N₂ passed through a powdered specimen reveals that after 40 to 80 minutes only 75 cm³ of H₂ are sorbed at 100 °C, while at 110°C the volume is 140 cm³, and at 150 °C it increases to over 900 cm³ as shown in Figure 6. The extent of

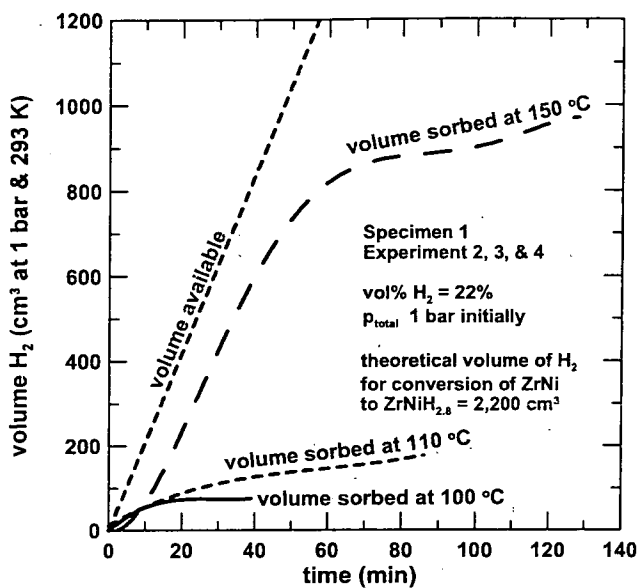


Fig. 6 Impact of temperature on capture of H_2 with ZrNi

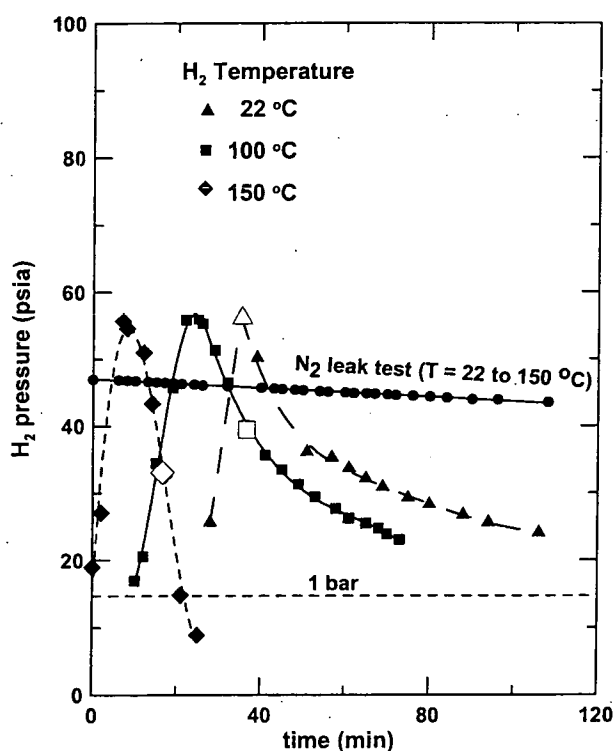


Fig. 7 - Impact of temperature and pressure on sorption of H_2 . Initial mass of as received specimen was 12.89 g.

conversion of ZrNi to its hydride, for all experiments run at 150 °C and at an initial total pressure of 1 bar with $p_{H_2} \approx 0.2$ bar, was 30 to 45%. The data in Figure 6 also reveal that the rate of sorption at 150 °C retains a significantly higher value, over a significant greater volume of H_2 sorbed, than observed at the lower temperatures.

The impact of temperature on the sorption process was also examined at higher pressures using a closed system. These experiments were run with a single specimen that was pretreated by heating to 300 °C under flowing N_2 for a minimum of 16 hours, and then cooled to room temperature prior to exposure to H_2 . Once the specimen was at room temperature, the system was flushed with H_2 at 48 ccm for a period of 15 minutes to remove N_2 from the system as determined with

the GC. At the end of that period the exit stream was sealed and the system allowed to pressurize with H_2 to 55 psia before completely sealing the system. After pressurizing the system, the furnace temperature was raised to the desired value. During the entire process, pressure and temperature within the reactor were recorded as a function of time, and the results plotted in Figure 7. This process was identical for the 3 experiments. The large open symbol for each experiment in the figure represent the time at which the hydride furnace achieved the desired temperature. The results, in Figure 7, for experiments conducted at the lower temperatures are offset 10 and 28 minutes for purpose of clarity. The figure also contains information on the leak rate that was obtained with N_2 at 22 °C, 100 °C and 150 °C, and used to make minor correction to the slope of the lines plotted in Figure 8.

The intent of these experiments was to obtain the rate of reaction as a function of P_{H_2} . By obtaining the derivative, dP_{H_2}/dt , it is possible to relate the rate moles of H_2 consumed per unit time through the ideal gas law where

$$dP_{H_2}/dt = (RT_{ef}/V)dn_{H_2}/dt. \quad (2)$$

Although the temperature of the gas within the pressurized volume varies, there is an effective temperature, T_{ef} , that satisfies the ideal gas law.

Proof that an effective temperature exists is obtained by dividing the total volume into z volume elements, where z is a large number. Each volume element is small enough, such that the ideal gas law accurately represents each element. The size of each volume element can vary, but the number of moles of gas in each element is constant, and represented by Δn . By writing the ideal gas law for each volume element and summing the equations yields:

$$(P_{H_2} V_1 = \Delta n R T_1) + (P_{H_2} V_2 = \Delta n R T_2) + \dots = \left(P_{H_2} \sum_{i=1}^z V_i = \Delta n R \sum_{i=1}^z T_i \right) \quad (3)$$

$\sum_{i=1}^z V_i$ is the total pressurized volume, and $\sum_{i=1}^z T_i$ can be replaced by zT_{ef} , leading to

$$P_{H_2} V = z \Delta n R T_{ef} \quad (4)$$

The total moles, n_{H_2} , in the system is equal to $z \Delta n$ and thus equation 4 becomes

$$P V = n_{H_2} R T_{ef} \quad (5)$$

from which equation 2 was obtained.

In this investigation, the effective temperature for all 3 experiments was approximately room temperature. The leak test with N_2 , conducted at 22 °C, 100 °C, and 150 °C, revealed both little change in pressure with respect to time and almost no difference in volume for the 3 temperatures as shown in Figure 7. That result reflects the fact that the free space in the hydride reactor is small in comparison to the total pressurized volume. Since the pressure did not increase significantly with increasing temperature during the leak test, and since the majority of the volume of the pressurized system was at room temperature, T_{ef} was approximately 293 K. While an effective temperature is used to convert the change in

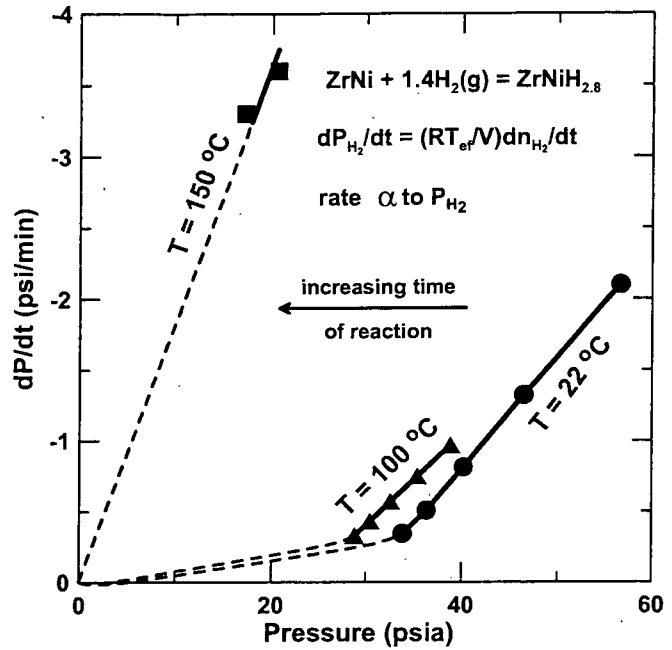


Fig. 8 - Rate of sorption as function of the pressure of H_2 . Data points indicate values of dP_{H_2}/dt obtained from the curves in Figure 7 and corrected for the leak rate.

pressure to the change in moles in equation 2, the temperatures reported in Figures 7 and 8 reflect the actual values within the hydride reactor.

Normally, experiments are run at a fixed pressure of H_2 to evaluate kinetic processes. A constant value of P_{H_2} could not be achieved with the closed system, nor with a flowing gas in the open system. The pressure drops in the closed system as a result of H_2 consumption, while with the flowing gas, the pressure drop across the bed increases significantly with hydride formation. In spite of this drawback, the closed system with the pressurized reactor provided some significant results. Values of dP_{H_2}/dt were found to vary linearly with P_{H_2} as shown in Figure 8, indicating that the rate of reaction is 1st order with respect to the concentration of H_2 . Since pure H_2 was used in these experiments, the likely rate controlling mechanisms are chemical or solid-state diffusion of hydrogen through a protective layer of hydride. The latter mechanism would involve diffusion of monatomic hydrogen through the hydride layer³, and thus the rate of reaction would be proportional to $\sqrt{P_{H_2}}$. Since that dependency was not observed, it appears that at 22 °C and 100 °C the rate of reaction is initially controlled by a chemical step that is 1st order with respect to P_{H_2} .

The lines in Figure 8 must pass through the origin, as the rate of reaction must go to 0 as P_{H_2} goes to 0. Thus, the slopes of the lines obtained at 22 °C and 100 °C must change at lower values of P_{H_2} , suggesting a change in mechanism. Since no hydride layer exist initially, the change in mechanism is probably due to a shift from chemical control to that of diffusion of H through the hydride layer. Such a change in mechanism must result in decreasing slope of the line as P_{H_2} declines due to growth of the hydride

layer that increases the resistance to diffusion. Such a change in slope can be projected for the results obtained at 22 and 100 °C.

Unfortunately, the data at 150 °C are severely limited, but suggest the possibility of chemical control, as a straight line emanating from the origin can be passed through the experimental points. It is not possible, using the 2 data points, to project a change in slope of the line, such as that observed at the lower temperatures. That result, and the fact a straight line passes through the origin and the data points in Figure 8 at 150 °C, implies that the rate of reaction is limited solely by a chemical process. However, based on the results obtained at the lower temperatures, formation of the hydride layer encapsulating ZrNi particles is expected to eventually limit the rate of reaction. Given the greater volume of H₂ reacted at 150 °C, transfer from chemical control to diffusion control was expected. For a chemical step to be the sole rate controlling process at 150 °C, there must be a significant increase in the diffusivity of hydrogen in the hydride with increasing temperature. Such a dramatic increase in the diffusion of hydrogen through the hydride layer may occur due to swelling, or, as in metals, there may be a change in mechanism involving diffusion of hydrogen that occurs with increasing temperature. For metals, 4 different mechanisms have been proposed to explain the increasing values of the diffusivity of hydrogen with increasing temperature.³

The volume of H₂ sorbed with the closed system at 22 °C was experimentally determined to be 550 cm³. Using that volume, the ideal gas law with the effective temperature, and the pressure differential corresponding to the volume of gas sorbed, it was possible to calculate the pressurized volume (or free space) in the system as being 780 cm³. With knowledge of the free space it was possible to compute the volume of H₂

sorbed for pressurized experiments conducted at 100 °C and 150 °C as 830 and 1150 cm³ respectively.

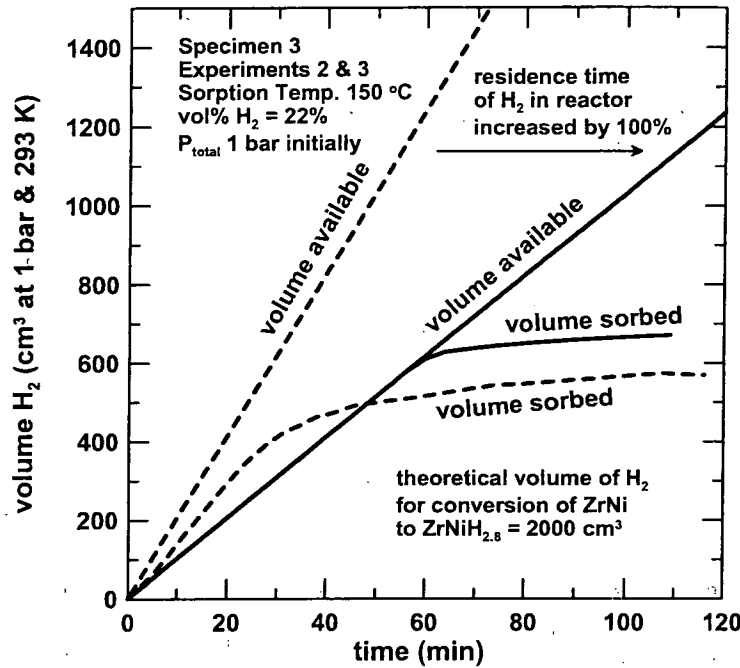


Fig. 9 – Impact of residence time on sorption of H₂.

Increasing the residence time of H₂ in the reactor with a flowing system significantly impacts the extent of sorption. The residence time was doubled by reducing the superficial velocity from 2.1 cm/s 1.05 cm/s while maintaining the mole fraction of H₂ in the gas at approximately 0.2. The impact of increasing the residence time is presented in Figure 9,

where it is seen that 100% of the hydrogen is sorbed for 60 minutes. The results of that experiment are compared to results obtained with the same specimen but at the shorter residence time. Increasing the residence time closes the gap between the lines for volume available and volume sorbed.

ZrNi is an excellent candidate for sorption of lunar H₂ as ZrNiH_{2.8}. It self activates at room temperature at P_{H_2} equal to 55 psia, and at 100 °C with p_{H_2} equal to 0.2 bar. Furthermore, the hydrogen can be fully desorbed at 300 °C. Both the sorption rate and volume of H₂ sorbed, with p_{H_2} fixed at 0.2 bar, were found to significantly increase with increasing temperature from 100 to 150 °C. Raising P_{H_2} to 55 psia in a closed system

produced the same result, namely that both the rate and volume of H₂ sorbed also increased with increasing temperature. Doubling the residence time by decreasing the flow rate achieved the desired result of 100% sorption for a period of 60 minutes.

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References

1. D. R. Gaskell, Introduction to Metallurgical Thermodynamics, 2nd ed., McGraw-Hill, New York, 1981, pp. 230-232.
2. Hydride Materials Data Base,
<http://hydpark.ca.sandia.gov/HydrideMaterialListing.html>, Sandia National Laboratories, May, 2002
3. Y. Fukai and H. Sugimoto, Advances in Physics, vol. 34, No. 2, 1995, pp. 263-326.